

PATENT SPECIFICATION

(11) 1 538 093

1 538 093

(21) Application No. 2263/76 (22) Filed 21 Jan. 1976
 (23) Complete Specification filed 20 Dec. 1976
 (44) Complete Specification published 17 Jan. 1979
 (51) INT CL² C08J 9/08
 (52) Index at acceptance
 C3C 100 101 106 109 113 117 416 418
 (72) Inventor IAN ROBERT WHITESIDE



(54) UREA-FORMALDEHYDE RESIN COMPOSITIONS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and 5 the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to urea-formaldehyde resin compositions, to foams 10 made from these compositions, and to a method of making such foams.

Foams made from urea-formaldehyde 15 resins are well known and are commonly used to fill the cavity walls of houses and other buildings and thereby act as insulants.

The foams are often prepared by mixing 20 an acid hardener with a surfactant, whipping the mixture into a foam by means of compressed air, and adding the resin to the foam, when it cures rapidly. Such foams are of low density and have a very limited mechanical strength. Foams have also been prepared by mixing a urea-formaldehyde 25 resin with a blowing agent which liberates a gas, either on heating or on treatment with an acid, and causing that gas to be liberated while the resin cures. Such foams generally have a greater density and mechanical 30 strength than those prepared using compressed air as the blowing agent. Typical such mixtures are described in British Patent Specifications Nos. 881726, 35 897067, and 978623. The blowing agents described in these Specifications include ammonium, alkali metal, and guanidine carbonates.

Thus, in Specification No. 881726, a 40 substrate is provided with a foamed or porous coating by fluidising the material to be foamed in a dry pulverulent form; heating the substrate to a temperature at least as high as the softening point of the material; allowing the fluidised material to flow against the heated substrate, thereby 45 forming a softened mass of the material thereon; producing gaseous material within the resultant melt; and setting the melt with the gaseous material therein, thereby forming a foam. Amongst many materials

listed from which foams may be produced are urea-aldehyde resins, and amongst the various kinds of blowing agents mentioned are inorganic materials such as ammonium and sodium bicarbonates.

Specification No. 897067 relates to a 50 method for improving both the structure and fertility of soil which comprises tilling into the soil a granular or coarsely-subdivided product comprising or consisting of a urea-formaldehyde condensation product hardened or cured in the form of either a foam or other low density material of extended or expanded structure. Amongst ways of producing a foamed or expanded structure is suggested blending a fusible, heat-reactive urea-formaldehyde powder resin with blowing agents or other gas-liberating substances, e.g., guanidine carbonate, together with a 55 hardening agent and any other additives, and sintering or melting to a mass which foams and hardens.

Specification No. 978623 provides a heat-insulating, potentially intumescent cellular material comprising a cured, cellular, resinous condensation product derived 60 from at least one aminoplast precondensation product, said material having substantially uniformly distributed throughout the cell walls thereof an intumescing agent and at least one saccharide or a polyol containing at least four hydroxyl groups, said intumescing agent being present in an amount of at least 65 5% of the weight of the aminoplast precondensate. Intumescing agents listed are sulphamic acid and its ammonium salt, ammonium chloride and bromide, ortho-, meta-, and pyro-phosphoric acid, and ammonium amine, and salt-forming amide salts of any of these acids. To form the 70 cured cellular resinous product there may be used several different kinds of blowing agent, such as a substance which reacts with a part of an acid or acid salt present in the mixture as curing agent or with a part of an acid-reacting intumescing agent which 75 effects the curing of the resinous

50

55

60

65

70

75

80

85

90

95

5 precondensation product and simultaneously liberates a gas. Such a substrate is a carbonate, and alkali metal, ammonium, magnesium, calcium, barium, nickel, and manganese carbonates are cited as being suitable.

10 Use of carbonates or bicarbonates of ammonia, alkali metals or amines in synthetic resins such as urea-formaldehyde resins has been proposed in British Patent

15 Specification No. 448102. Cellular grinding bodies (such as grinding discs) were produced by mixing grains of an abrasive material, substance which evolves a gas on

20 being heated, such as a carbonate, and a precondensed, heat-curable synthetic resin, and heating for 1 to 3 hours the mixture in a mould with a perforated cover. In the example, ammonium carbonate liberated a

25 gas which escaped, and the volume of the mixture increased by about 50%, it becoming porous or cellular. No mention was made of specific amine carbonates which could be used, and no difference was noted in the behaviour of amine carbonates and other carbonates, such as those of alkali metals.

30 We have now found that urea-formaldehyde resins may be simultaneously foamed and rendered capable of intumescing, i.e., of expanding still further when heated to carbonising temperatures.

35 By employing certain amine carbonates and certain strong acids. Such intumescence serves to insulate the underlying material from the effects of further heat. The foams therefore form an effective barrier to fires if incorporated into fire-retardant doors, panels, etc.

40 That these foams intumesc is surprising, since foams made by whipping air into the curing mixture of a urea-formaldehyde resin and (ortho)-phosphoric acid contract markedly when heated and leave a small amount of ash, while urea-formaldehyde foams made by incorporating alkali metal carbonates and adding a strong acid, i.e., orthophosphoric acid, char when heated and show no tendency to intumesc.

45 This invention therefore provides aqueous compositions comprising (i) a urea-formaldehyde resin,

50 (ii) an effective amount of a strong (as herein defined) phosphorus acid as hardener therefor, and

55 (iii) a carbonate of an aliphatic, araliphatic, heterocyclo-aliphatic or heterocyclic amine having at least one primary or secondary amino group and from 1 to 12 carbon atoms.

60 There is also provided a method for making a synthetic resin foam which comprises mixing together in the presence of water a urea-formaldehyde resin and a carbonate of an aliphatic, araliphatic,

65 heterocyclo-aliphatic or heterocyclic amine having at least one primary or secondary amino group and from 1 to 12 carbon atoms, adding an effective amount of a strong (as herein defined) phosphorus acid to the mixture, and allowing the mixture to foam and cure.

70 There are further provided foams made by this method.

75 Urea-formaldehyde resins suitable for use in accordance with the present invention are commercially available. They are usually prepared by the reaction of 1 mol of urea with 1.8 to 2.3 mols of formaldehyde under alkaline, followed by acidic, conditions, neutralisation, and, optionally, addition of urea to give a final molar ratio of formaldehyde: urea (F:U) of 1.2 to 2.3:1. Resins preferred for use in this invention are those in which the F:U molar ratio is from 1.3 to 1.7:1.

80 Amines which are used, as their carbonates, in this invention are preferably aliphatic and contain at least one primary amino group and 1 to 6 carbon atoms. They may be substituted by one or more hydroxyl groups, especially by one or two hydroxyl groups. Monoethanolamine and diethylenetriamine, as their carbonates, are particularly preferred.

85 90 95 100 105 110 115 120 125

As is well known, when an amine is treated with carbon dioxide, the product is usually not a pure compound but is a mixture of various components. The terms 'amine carbonate' and 'carbonate of an amine' where amine has the meaning herein defined are used herein to encompass both the mixture resulting from this reaction and also the pure carbonate.

105 A phosphorus acid used to cure and foam the urea-formaldehyde resins must be a strong acid, by which is meant one having an acid strength ($-\log K_A$) of 5 or less. We prefer to use (ortho)phosphoric acid but, e.g., metaphosphoric, pyrophosphoric, phosphorous, and polyphosphoric acids may also be used.

110 115 120 125

If desired, a small amount of a surfactant, preferably up to 0.5% by weight of the total composition, may be incorporated into the compositions of the present invention in order to modify the physical properties of the resultant foams. Surfactants are not essential however, and very satisfactory foams may be prepared in their absence.

The urea-formaldehyde resin may be present as an aqueous dispersion of the spray-dried powder, but more conveniently as an aqueous syrup, a form in which the resins are commonly supplied commercially.

The amount of urea-formaldehyde resin (including water in the resin as supplied or added) in the compositions is usually from

65 to 90% by weight, 70 to 85% by weight being preferred, calculated on the combined weight of the components (i), (ii), and (iii), and water. Liquid urea-formaldehyde resins commercially available usually having a resin-forming solids content of 60 to 75% by weight, the corresponding amounts of urea-formaldehyde resin on a theoretical resin-forming solids basis are 39 to 67.5%, preferably 42 to 63.5%. (By resin-forming content is meant the percentage residue left after a 1 g sample of the material has been heated in a 5 cm diameter dish in an oven at 120°C for 3 hours at atmospheric pressure). The amount of amine, present as its carbonate, is usually from 0.8 to 4.0%, and preferably 1.2 to 3.0%, by weight calculated on the combined weights of (i), (ii), and (iii) and water. Amine carbonates can be prepared by passing carbon dioxide gas or putting solid carbon dioxide into the amine, which is usually in aqueous or organic solution, until saturated, and are generally added in solution. The amount of the phosphorus acid used is not critical, provided there is sufficient to liberate carbon dioxide from the carbonate and to lower the pH of the mixture sufficiently for the resin to harden. Generally, the acid constitutes from 10 to 20% by weight of the composition, i.e., calculated on the combined weights of components (i), (ii), and (iii) and water, 12 to 16% by weight being preferred. The acid may be added in concentrated form or, more conveniently, diluted with water. When water is incorporated in the mixture, either as a solvent for the amine carbonate or as diluent for the acid or the resin it usually constitutes up to 15% by weight of the composition, preferably from 5 to 10% by weight, not including any water already present in the urea-formaldehyde resin. The foams of the present invention may be prepared batchwise by mixing all of the ingredients except for the acid and, when a homogeneous mixture is obtained, adding the acid, mixing briefly, and allowing the foaming to take place. When working continuously, the resin and a solution of the amine carbonate, optionally containing the surfactant, are mixed in a continuous mixer and, just prior to ejection from the mixer, the acid is fed into the mixer. Foaming takes place outside the mixing head, as distinct from urea-formaldehyde foams manufactured by incorporation of air into the mixture, in which the foam is formed within the mixing head. The invention is illustrated by the following Examples, in which all parts and percentages are by weight, unless otherwise indicated. The resins used in these Examples were as follows:

Resin I
A precursor resin having an F:U molar ratio of 1.9:1 and a kinematic viscosity at 99—100°C of $3.3 \times 10^{-6} \text{ m}^2/\text{sec}$ was made by heating 37% aqueous formaldehyde solution and urea to refluxing for 30 minutes with sufficient dilute sodium hydroxide solution to bring the pH to 8, then adjusting the pH to 5 with 10% aqueous formic acid and continuing to heat to refluxing point until the resin had the desired viscosity. The product was evaporated at 10 mm mercury and 40°C until the resin-forming solids content was 67% and then, at room temperature, urea was added to bring the F:U molar ratio to 1.4:1. The mixture was left at room temperature for 24 hours before being used, to reach equilibrium.

Resin II
denotes a urea-formaldehyde resin having an F:U molar ratio of 1.7:1, prepared by addition at room temperature of urea to the same precursor resin used in the preparation of Resin I. The mixture was left for 24 hours at room temperature before being used.

Resin III
A precursor resin having an F:U molar ratio of 1.9:1 and a kinematic viscosity at 99—100°C of $4.25 \times 10^{-6} \text{ m}^2/\text{sec}$ was made by the method described under Resin I. Urea was added as before, to bring the F:U molar ratio to 1.6:1. The mixture was left at room temperature for 24 hours before being used.

Resin IV
A precursor resin having an F:U molar ratio of 1.9:1 and a kinematic viscosity at 99—100°C of $3.5 \times 10^{-6} \text{ m}^2/\text{sec}$ was made by the method described under Resin I. Urea was added as before, to bring the F:U molar ratio to 1.7:1. The mixture was left for 24 hours at room temperature before being used. The resin-forming solids content of Resins I to IV were, 68 to 69%.

EXAMPLE 1
Resin I (78.5 parts) was mixed thoroughly in an open beaker with an aqueous solution of monoethanolamine carbonate, prepared by passing carbon dioxide into a 30% aqueous solution of monoethanolamine (1.44 parts) until an exothermic reaction no longer ensued. Orthophosphoric acid (100%, 12.6 parts) in water (7.2 parts) was added to the mixture and after stirring vigorously with a mechanical stirrer for 1 to 2 seconds, the stirrer was removed. The mixture commenced foaming almost immediately, and foam formation was complete after 2 minutes. The foam was then removed from

the beaker and allowed to dry. A sample was heated in a bunsen flame, where it intumesced readily.

EXAMPLE 2

5 Example 1 was repeated but surfactant (0.2 part) was included in the resin-amine carbonate mixture. The surfactant, which was neutral and hydrophilic, was an adduct of a mixture of primary aliphatic long chain amines having 16 to 18 carbon atoms (1 mol) with ethylene oxide (70 mols).

10 The resultant foam had a greater volume than that produced in Example 1, but the degree of intumescence, i.e., the amount by 15 which the foam increased in volume on being heated in a flame, although considerable, was not as great.

EXAMPLE 3

20 Example 1 was repeated, replacing the monoethanolamine carbonate with an aqueous solution of diethanolamine carbonate, prepared from 2 parts of diethanolamine as a 30% aqueous solution. The resultant foam was similar to that 25 prepared in Example 1 but the degree of intumescence was slightly less.

EXAMPLE 4

Example 1 was repeated, replacing the monoethanolamine carbonate by 30 a) a mixture of 2,2,4 - trimethylhexane - 1,6 - diamine and 2,4,4 - trimethylhexane - 1,6 - diamine carbonates (prepared from 1.36 parts of the amine mixture) or b) diethylenetriamine carbonate (prepared from 2.87 parts of the amine) or 35 c) *N* - (2 - aminoethyl)piperazine carbonate (prepared from 1.36 parts of the amine).

In all three experiments the resultant 40 foams and their intumescence were satisfactory, the results obtained using diethylenetriamine carbonate being particularly good.

EXAMPLE 5

45 Example 1 was repeated, replacing Resin I by Resin II (84.2 parts), Resin III (84.2 parts), or Resin IV (81.5 parts). In all cases satisfactory foams were obtained.

When, for purposes of comparison, 50 Example 1 was repeated with carbonates prepared from triethanolamine (i.e., a solely tertiary amine) or a poly(oxypropylene diamine) having an average molecular weight of about 2000, satisfactory foams could not be produced. For further comparison, the procedure of Example 1 was repeated, using calcium, sodium, or potassium carbonate (3.1 parts), with 5.3 parts of orthophosphoric acid and 60 5.3 parts of water.

Although in these cases foams were

produced, they did not intumesce on burning but merely charred.

EXAMPLE 6

65 Example 1 was repeated, the orthophosphoric acid being replaced by 10.5 parts of orthophosphorous acid (100%) or by 31 parts of metaphosphoric acid (100%), i.e., equivalent amounts on a hydrogen ion basis. In both cases the foam 70 intumesced strongly on being heated.

75 For purposes of comparison, Example 1 was repeated using concentrated hydrochloric acid (21.7 parts), concentrated sulphuric acid (13.6 parts), or toluene - *p* - sulphonic acid (13 parts). In each case satisfactory foams were produced, but, on being heated strongly, the foams did not intumesce.

WHAT WE CLAIM IS:—

80 1. Aqueous compositions comprising
(i) a urea-formaldehyde resin,
(ii) an effective amount of a strong (as
herein defined) phosphorus acid as
hardener therefor, and
(iii) a carbonate of an aliphatic,
araliphatic, heterocyclo-aliphatic or
heterocyclic amine having at least one
primary or secondary amino group and
from 1 to 12 carbon atoms.

85 2. Compositions according to claim 1, in
which the urea-formaldehyde resin has a
molar ratio of formaldehyde to urea of from
1.2 to 2.3:1.

90 3. Compositions according to claim 2, in
which the said molar ratio is from 1.3 to
1.7:1.

95 4. Compositions according to any
preceding claim, in which the carbonate is
of an aliphatic amine containing at least
one primary amino group and 1 to 6 carbon
atoms.

100 5. Compositions according to claim 4, in
which the aliphatic amine is substituted by
one or more hydroxyl groups.

105 6. Compositions according to claim 4, in
which the aliphatic amine is
monoethanolamine or diethylenetriamine.

110 7. Compositions according to any
preceding claim, in which the urea-
formaldehyde resin comprises from 39 to
67.5% by weight, expressed as 100% resin-
forming solids content (as herein defined),
calculated on the combined weights of (i),
(ii), and (iii).

115 8. Compositions according to claim 7, in
which the urea-formaldehyde resin
comprises from 42 to 63.5% by weight,
calculated on the same basis.

120 9. Compositions according to any
preceding claim, in which the amine, the
carbonate of which is employed as
component(iii), comprises from 0.8% to 4%

by weight, calculated on the combined weights of (i), (ii), and (iii) and water.

10. Composition according to claim 9, in which the said amine comprises from 1.2 to 5 3% by weight, calculated on the same basis.

11. Compositions according to any preceding claim, in which the acid (ii) is metaphosphoric acid, pyrophosphoric acid, phosphorous acid, or a polyphosphoric acid.

10 12. Compositions according to any of claims 1 to 10, in which the acid is orthophosphoric acid.

15 13. Compositions according to claim 1, substantially as described herein.

14. Compositions according to claim 1, substantially as described in any of Examples 1 to 5.

20 15. Compositions according to claim 1, substantially as described in Example 6.

16. A method for making a synthetic resin foam which comprises mixing together in the presence of water a urea-formaldehyde resin and a carbonate of an aliphatic, araliphatic, heterocyloaliphatic or heterocyclic amine having at least one 25

primary or secondary amino group and from 1 to 12 carbon atoms, adding an effective amount of a strong (as herein defined) phosphorus acid to the mixture, and allowing the mixture to foam and cure.

17. A method according to claim 16, in which the foaming mixture comprises a composition as claimed in any of claims 2 to 11, 13, and 15.

18. A method according to claim 16, in which the foaming mixture comprises a composition as claimed in claim 12 or 14.

19. A method according to claim 16, substantially as herein described.

20. A method according to claim 16, substantially as described in any of Examples 1 to 5.

21. A method according to claim 16, substantially as described in Example 6.

22. Foams made by the method of any of claims 16, 17, 19, and 21.

23. Foams made by the method of claim 18 or 20.

T. SHARMAN,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.